ONE-PART GEOPOLYMERS VERSUS ORDINARY PORTLAND CEMENT (OPC) Mortars: DURABILITY ASSESSMENT

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ABSTRACT
Investigations on the field of geopolymeric binders, state that this new material is likely to have high potential to become an alternative to Ordinary Portland cement (OPC). Recent results on the Life Cycle Analysis (LCA) of geopolymers they have a lower impact on global warming than OPC but on the other side they have a higher environmental impact regarding other impact categories. Lower CO_2 emissions geopolymers are therefore needed. Classical two part geopolymers could be made more eco-efficient with a lower carbon dioxide footprint if the use of sodium silicate is avoided. Besides current geopolymeric mixes can suffer from efflorescence originated by the fact that alkaline and/or soluble silicates that are added during processing cannot be totally consumed during geopolymerisation. Therefore new and improved geopolymer mixes are needed. One-part geopolymers (sodium silicate free) were described by the first time in 2008 still a lot of issues remain unexplained about them. This paper compares the durability performance of one-part geopolymers with OPC mortars. The obtained results revealed that replacing 70% Portland cement by 58.3% Fly ash, 4% calcined stuff and 7.7% calcium hydroxide results in satisfactory and promising results in durability tests.

Keywords: Geopolymers; ordinary Portland cement; fly ash; durability performance.

INTRODUCTION

With an annual production of almost 3 Gt Ordinary Portland cement (OPC) is the dominant binder of the construction industry [1]. The production of one tonne of OPC generates 0.55 tonnes of chemical CO_2 and requires an additional 0.39 tonnes of CO_2 in fuel emissions for baking and grinding, accounting for a total of 0.94 tonnes of CO_2. Other authors [2] reported that the cement industry emitted in 2000, on average, 0.87 kg of CO_2 for every kg of cement produced. As a result the cement industry contributes about 7% of the total worldwide CO_2 emissions [3]. The projections for the global demand of Portland cement show that in the next 40 years it will have a twofold increase reaching 6 Gt/year. The urge to reduce carbon dioxide emissions and the fact that OPC structures which have been build a few decades ago are still facing disintegration problems points out the handicaps of OPC. Portland cement based concrete presents a higher permeability that allows water and other aggressive media to enter leading to carbonation and corrosion problems. The early deterioration of reinforced concrete structures based on ordinary Portland cement (OPC) is a current phenomenon with significant consequences both in terms of the cost for the rehabilitation of these structures, or even in terms of environmental impacts associated with these operations. Research works [4-8] carried out so far in the development of geopolymers showed that much has already been investigated and also that an environmental friendly alternative to Portland cement is rising.
Besides the durability of geopolymers is still a subject of some controversy [9]. While Duxon et al. [10] state this is the most important issue on determining the success of these new materials and other authors [11] mention that the fact that samples from the former Soviet Union that have been exposed to service conditions for in excess of 30 years showing little degradation means that geopolymers do therefore appear to stand the test of time. But since those materials were of the (Si+Ca) type that conclusion cannot be extended to geopolymers defined as "alkali aluminosilicate gel, with aluminium

and silicon linked in a tetrahedral gel framework" [12]. On the other side Juenger et al. [1] argue that "The key unsolved question in the development and application of alkali activation technology is the issue of durability" and more recently Van Deventer et al. [13] recognized that "whether geopolymer concretes are durable remains the major obstacle to recognition in standards for structural concrete". Efflorescences is an important drawback of two part geopolymers that so far has received very little attention. This phenomenon is influenced by several causes like the reactivity of the alumino-silicate, the mix composition and the curing conditions. According to Skvara et al. [14,15] the bond between the sodium ions (Na+) and the aluminosilicate structure is weak and that explains the leaching behaviour. Kani et al. [16] showed that efflorescences can be reduced either by the addition of alumina-rich admixtures or by hydrothermal curing at temperatures of 65 ºC or higher. These authors found that the use of 8% of calcium aluminate cement greatly reduces the mobility of alkalis leading to minimum efflorescences (this cement has 28% of CaO). These results are very important because they constitute a step back in the development of geopolymers. For one the use of hydrothermal curing has serious limitations for on-site concrete placement operations. On the other hand the use of calcium based mixtures reduces the acid resistance and raises the chances for the occurrence of ASR. This means that this subject merits further investigations. One-part geopolymers represent a key event on geopolymer technology having been described by the first time in 2008. In this work, obtained experimental results from durability tests on a novel kind of mixes termed one-part geopolymers are presented.

EXPERIMENTAL WORK

MATERIALS

The composition of dry mix in this study was: ordinary Portland cement (OPC), fly ash, kaolin, sodium hydroxide, calcium hydroxide, water and superplasticizer (SP). A mixture of kaolin and sodium hydroxide which is calcined in a furnace at 650 ºC during 140 minutes. The cooled mixture is called calcined stuff. The OPC used was type 42,5 R with a clinker content between 95-100% and with a specific weight of 3.15 g/cm3 and a Blaine fineness of 3842 cm2/g. The SP was used to maintain a uniform consistency between the different mixes. The chemical composition of the fly ash complies with the minimum requirements indicated in EN-450-1 [16] for being used as a partial replacement of cement in concrete. Based on this standard the fly ash was categorized in class B and group N for the loss of ignition and fineness, respectively and it has a specific weight of 2.42 g/cm^3.

Table 1. Mixture proportions (%)

Name	OPC	Fly ash	$Ca(OH)_2$	Calcined stuff	Water	SP	Sand
OPC 100	100	----	----	-----	35	0.8	80
OPC 70 – FL 30	70	30	----	-----	35	0.8	80
OPC 30-FL 58.3-CH 7.7-CS 4	30	58.3	7.7	4	35	0.8	80
OPC 26-FL 58.3-CH 7.7-CS 8	26	58.3	7.7	8	35	0.8	80
OPC 18-FL 58.3-CH 7.7-CS 16	18	58.3	7.7	16	35	0.8	80

EXPERIMENTAL TESTS

Four experimental tests were carried out to evaluate the material behavior. The first stage was assigned to evaluate the material under compression while other stages were assigned to durability tests. In the second, third and fourth stages were conducted capillarity, immersion and acid attack tests, respectively. Hence, experimental producer of water absorption by immersion, water absorption by capillarity and resistance to acid attack are explained in the following:

Water absorption by immersion

Specimens were tested with 28 days curing. The specimens were immersed in water at room temperature for 24 hours. First the weight of the specimens while suspended by a thin wire and completely submerged in water is recorded as Wim (immersed weight). After that the specimens were removed from water, and placed for 1 min on a wire mesh allowing water to drain, then visible surface water is removed with a damp cloth and weight is recorded as Wsat (saturated weight). All specimens are placed in a ventilated oven at 105 ºC for not less than 24 hours and allowing that two successive weightings at intervals of 2 hours show an increment of loss not greater than 0,1% of the last previously determined weight of the specimen. The weight of the dried specimens is recorded as Wdry (oven-dry weight). Absorption coefficient is determined as following equation:

$$A(\%) = \frac{W_{sat} - W_{dry}}{W_{sat} - W_{im}} \times 100 \qquad (1)$$

Water absorption by capillarity
The test was done according to BS EN 1015-18:2002. For performing the capillary test, three specimens were cast and tested with dimension 100×100×100 mm^3. The preparation of test specimen was done as follows: after drying in an oven at 105°C for 60 hours, they are water proof along their lateral surface with a fine layer of silicon in order to reduce water evaporation and guaranty capillarity water absorption.

Resistance to acid attack
The cubic specimens with dimension 50×50×50 mm^3 were used to evaluate this criterion for acid attack. The weights of specimens were measured and then saturated in a solution which contains of 10% H_2SO_4 acid (In volume). The weights of specimens were measured for 7, 14, 28 and 56 days and the appearance of specimens were also observed.

RESULTS AND DISCUSSIONS
COMPRESSIVE STRENGTH
Figure 1 shows the compressive strength results. The reduction of OPC content leads to a high reduction on the compressive strength of the mortars. The slow hydration characteristics of fly ash contribute to explain that reduction. The mixture with just 30% OPC (and 58.3 fly ash, 7.7 calcium hydroxide and 4% calcined stuff) shows an almost 40% reduction in compressive strength when compare to the reference mixture. Since this mixture has a higher percentage reduction on OPC content this could mean that the addition of metakaolin and calcined sodium hydroxide could have compensated that reduction. However, the use of increase content in calcined stuff does not seem to compensate the OPC reduction. Thus meaning that the use of 4% calcined stuff seems to be an optimum content.

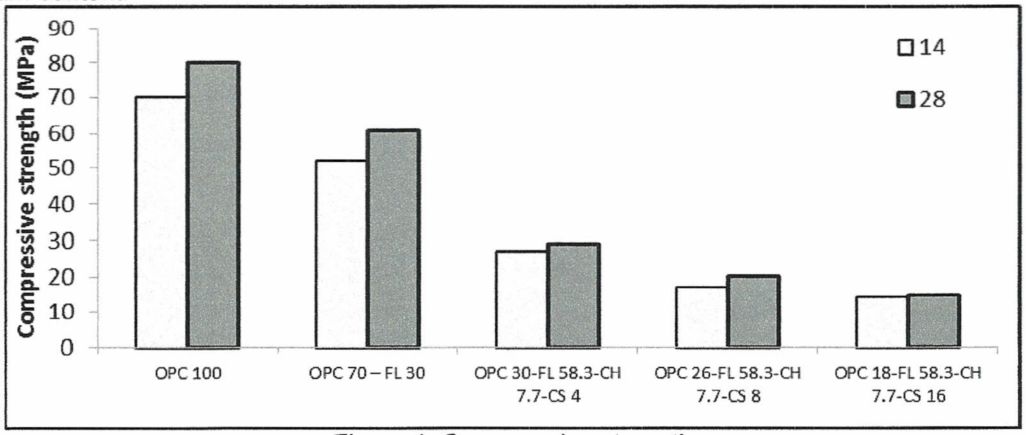

Figure 1. Compressive strength

WATER ABSORPTION BY IMMERSION
The results of water absorption by immersion are presented in Figure 2. Since all the mixtures have the same w/b ratio they should present a similar open porosity. So the differences between the several mixtures could be explained by the scatter data because they are small enough for that. Of course the different hydration products present in the different mixtures may contribute for the porosity differences but only in a very slight manner. That´s why the mixture already mention in the previous section as having a good compressive strength performance shows the lower open porosity.

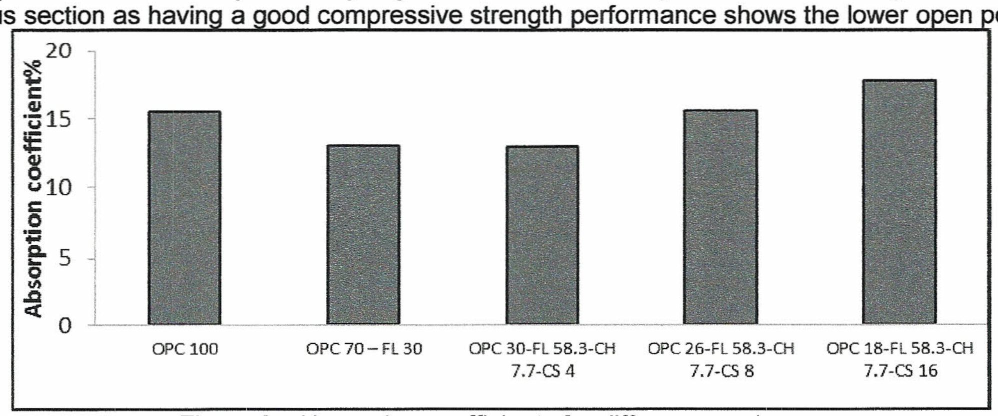

Figure 2. Absorption coefficients for different specimens

WATER ABSORPTION BY CAPILLARITY

Figure 3 shows the results of the capillary water absorption and the water absorption capillarity coefficients are showed in Figure 4. The reference mixture shows the best performance of them all. On the opposite side the mixture with 26% OPC 58.3 fly ash, 7.7 calcium hydroxide and 8% calcined stuff clearly shows a very high water absorption by capillarity even at early ages. Such performance is typical of a microstruture with a high amount of capillary pores. The three remaining mixtures show a similar capillary water absorption coefficient indicating a similar internal capillary pore network.

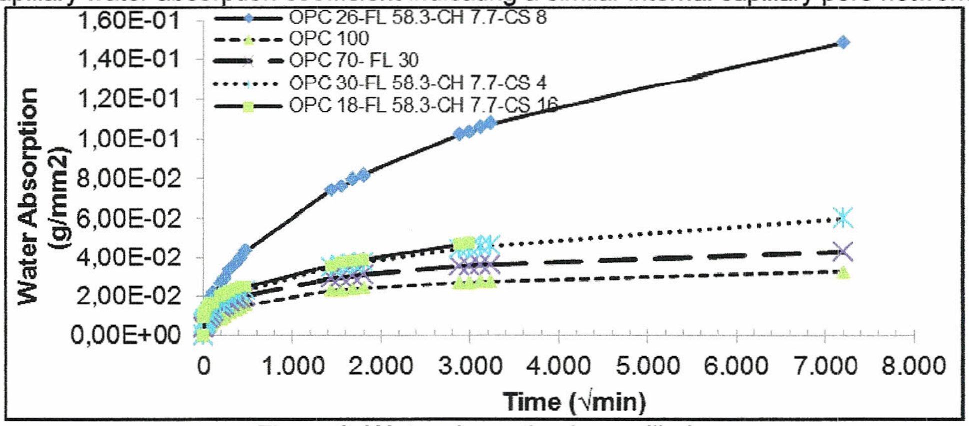

Figure 3. Water absorption by capillarity

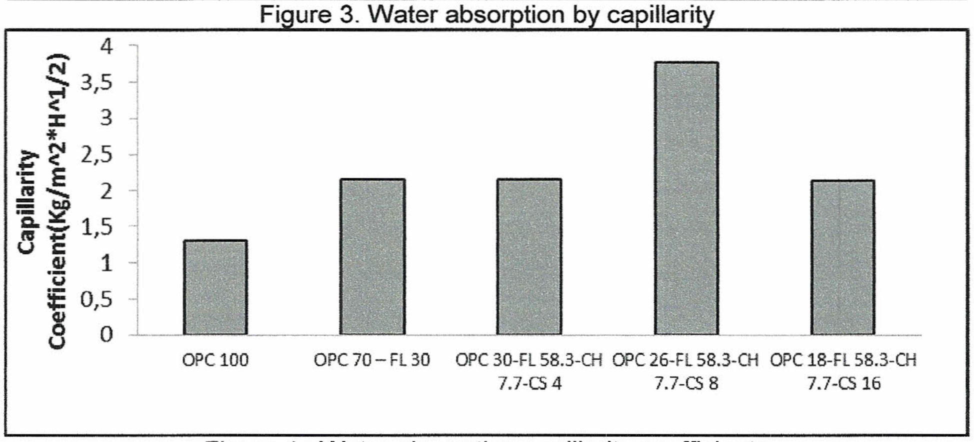

Figure 4. Water absorption capillarity coefficients

RESISTANCE TO ACID ATTACK

The results of mass loss for specimens exposed to 10% sulphuric acid solutions are shown in Figures 5.

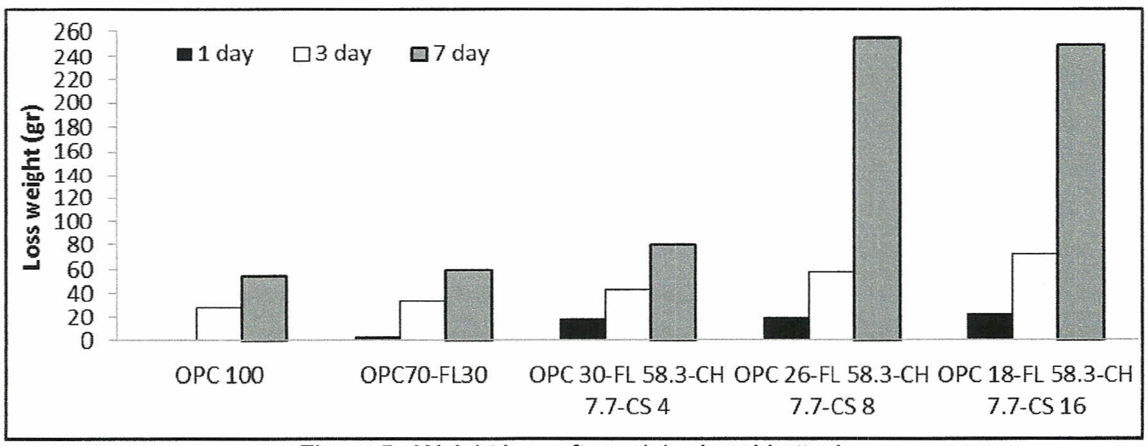

Figure 5. Weight loss after sulphuric acid attack

After 1 day the best results are shown by the reference mixture and also by the mixture in which 30% OPC was replaced by fly ash. Since the reference mixture has much lower capillary water absorption than the other mixes this means that in a short term the rate of acid ingress contributes to explain the observed results. However, this is not the case of the one part geopolymeric mixture with 8% calcined stuff because since it has the highest capillarity coefficient it should have a higher weigth loss than the other geopolymeric mixtures. After 3 days exposure to acid attack one can confirm that the weigth loss is proportional to the OPC content in the mixtures. A higher OPC content is associated to a lower weight loss. High pozzolan content mixtures showed lower resistance to acid attack this results do not confirm previous findings about the fact that the presence of pozzolanic admixtures was found to lower the detrimental effect of acid attack on concrete [17,18]. Probably because a denser microstructure typical of pozzolanic based mixtures were not yet formed by the time this mixtures were tested.

CONCLUSIONS

In this study, the durability of OPC mortars and the durability of one part geopolymer mortars were assessed using three different tests (water absorption by immersion, water absorption by capillarity and resistance to acid attack). Compressive strength results were also presented showing that the reduction of OPC content in the mortars leads to a high reduction on the compressive strength. The addition of fly ash is not enough to compensate the OPC reduction due to its slow hydration characteristics. In the geopolymeric mixtures the one with of 4% calcined stuff seems to correspond to a good compromise between a low OPC content and an acceptable compressive strength. The results of water absorption by immersion are very similar for all the mixtures which is due to the fact that they have the same w/b ratio. The capillary water absorption is very high for the one part geopolymeric mixtures with 8% calcined stuff indicating a microstructure with very high amount of capillary pores. The results of resistance to acid attack show that the weight loss is proportional to the OPC content in the mixtures.

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